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INFRARED SPECTROSCOPY

Introduction

The spectroscopy in the infrared region is concerned with the study of vibrating molecules. In the last chapter we could see that how the elasticity of bond length results in the vibration of molecule. The consequence of the elasticity is that the atoms in a molecule do not remain fixed in relative positions but vibrate about some mean position. It is due to vibration, molecules possess vibrational energy and this energy is quantised. When the molecule goes from one vibrational level to another energy is released or absorbed gives rise to a spectra called vibrational spectra. The wavelength region of the spectra is in the infrared. Hence the study of vibrational spectra is called infrared spectroscopy. This study gives us valuable information regarding molecular structure, symmetry, bond strength, inter and intramolecular interactions etc.

To develop the theory we have to make models to vibrating molecules. Here we shall deal with two models. One is simple harmonic oscillator model another one is the anharmonic oscillator model.

The vibrational energy of a diatomic molecule - (Harmonic oscillator model)

Here we assume that a diatomic molecule behaves like an oscillating spring - mass system. i.e., two masses m_1 and m_2 connected by a spring with force constant k . Here m_1 and m_2 are masses of two atoms and the elastic bond acts like a spring which obeys

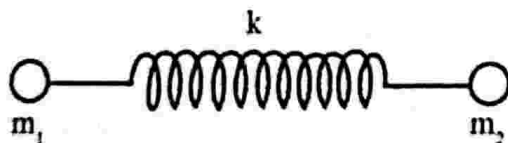


Figure 5.1

Hooke's law. If r_e is the distance between the two atoms in equilibrium. i.e., r_e is the equilibrium bond length. Suppose the bond is distorted from its equilibrium length r_e to new length r . The bond, like a spring, obeys Hooke's law. Then the restoring force f is given by

$$f = -k(r - r_e)$$

where k is the restoring force.

Then the potential energy of the system has the form

$$U = \frac{1}{2}k(r - r_e)^2$$

i.e., the energy curve is parabolic. This model of a vibrating molecule is called simple harmonic oscillator model. The frequency of such a motion is given by

$$\nu_0 = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

Here μ is called the reduced mass of the system given by

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

Now consider the diatomic molecule as a simple harmonic oscillator with potential energy $U = \frac{1}{2}k(r - r_e)^2$ and treat the problem quantum mechanically, we can arrive at the energy eigen values possessed by the diatomic molecule due to vibration. For this we have to solve the corresponding Schrodinger equation. After solving we arrive at the vibrational energy of such a harmonic system. This is given by

$$E_v = \left(v + \frac{1}{2}\right) h\nu_0, \quad v = 0, 1, 2, \dots \quad (1)$$

where v is called the vibrational quantum number.

Converting this into spectroscopic units, we have

$$\begin{aligned} \epsilon_v &= \frac{E_v}{hc} = \left(v + \frac{1}{2}\right) \frac{h\nu_0}{hc} = \left(v + \frac{1}{2}\right) \frac{\nu_0}{c} \\ \epsilon_v &= \left(v + \frac{1}{2}\right) \bar{\nu}_0 \quad \left(\frac{\nu_0}{c} = \frac{1}{\lambda} = \bar{\nu}_0\right) \end{aligned} \quad (2)$$

where $\bar{\nu}_0$ is the vibrational frequency of the oscillator in wave numbers. Its unit is cm^{-1} .

From equation (1) it is seen that the energy levels are equally spaced.

i.e.,
$$E_0 = \frac{1}{2} h\nu_0$$

$$E_1 = \frac{3}{2} h\nu_0$$

$$E_2 = \frac{5}{2} h\nu_0$$

$$E_3 = \frac{7}{2} h\nu_0$$

i.e., $E_3 - E_2 = E_2 - E_1 = E_1 - E_0 = \frac{1}{2} h\nu_0$. More over it is seen that the lowest energy possible is

$$E_0 = \frac{1}{2} h\nu_0.$$

This is called zero point energy. That is vibrational energy is not zero even at the lowest vibrational level. This shows that a molecule always vibrates.

The selection rule for the harmonic oscillator undergoing vibrational changes is

$$\Delta v = \pm 1$$

This shows that the transitions are allowed only to adjacent vibrational levels.

Vibrational energy changes will only give rise to an observable spectrum if the vibration can interact with radiation. i.e., if the vibration involves a change in the dipole moment of the molecule. Thus vibrational spectra will be observable only in heteronuclear diatomic molecules like HF, HCl, HBr etc. Homonuclear molecules like H_2 , N_2 and O_2 show no vibrational spectrum since they have no dipole moment.

From eqn (2) it is seen that

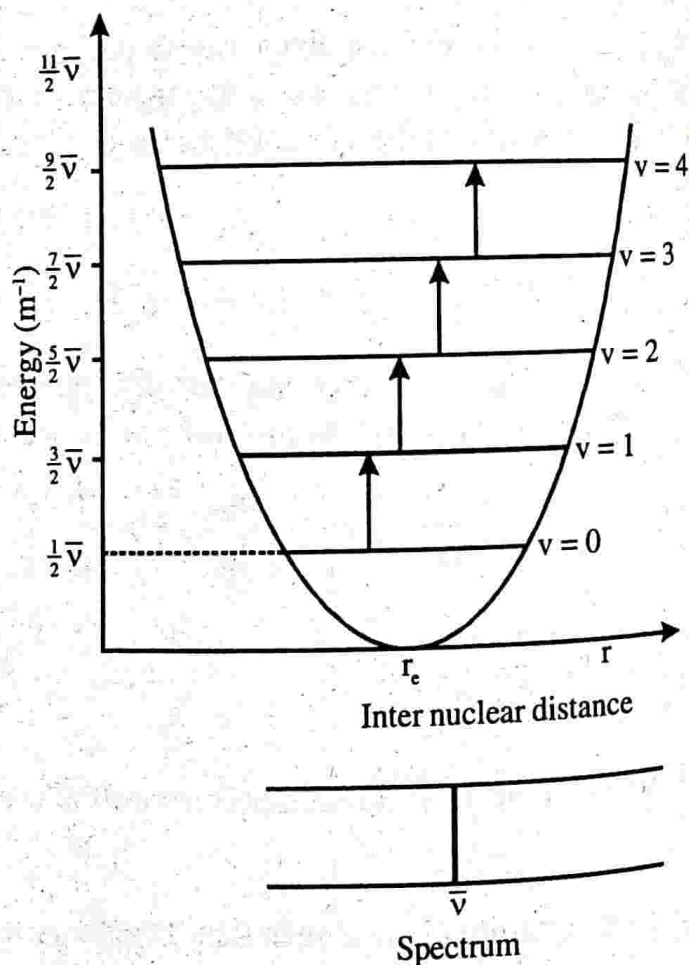


Figure 5.2

when a molecule goes from its vibrational level v to $v+1$, all the vibrational lines obtained from harmonic oscillator are of the same frequency. The allowed vibrational energy levels and transitions between them for a diatomic molecule undergoing simple harmonic motion are shown in figure.

In reality molecules do not obey the laws of simple harmonic motion. This is because real bonds, though which are elastic do not obey Hooke's law. So we have to resort to the second model - anharmonic oscillator model.

The anharmonic oscillator model

When we come to real molecules they do not obey exactly the laws of simple harmonic motion. This is because the real bond, though elastic, does not obey Hooke's law hence potential energy function will not be parabolic in nature. In order to obtain the experimentally observed spectra several potential energy functions have been suggested. One which was successful in its attempt was suggested by P.M. Morse and is called the Morse function and is given by

$$U = D_e [1 - \exp \{a(r_e - r)\}]^2 \quad \dots (3)$$

where D_e is called the dissociation energy and a is a constant for a particular molecule.

The idea of dissociation energy comes as follows. If the bond between atoms is stretched beyond a limit, there comes a point at which it will break - the molecule dissociates into atoms. This has also been incorporated in the potential energy function.

Put $r = \infty$ in the above equation, we get

$$U = D_e$$

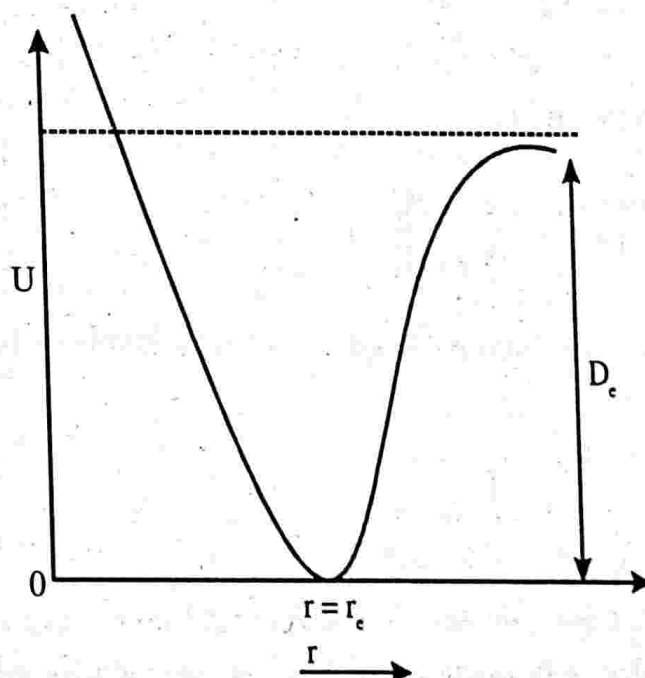


Figure 5.3

Hence the term dissociation energy. The graphical variation of U with r is given below.

From the equation, we get

$$r = r_e \text{ when } U = 0$$

when the two atoms are at equilibrium distance ($r = r_e$) the potential energy at equilibrium is zero, which is assumed.

Using the Morse function, solve the Schrodinger equation we get the vibrational energy levels as

$$\epsilon_v = \left(v + \frac{1}{2}\right) \bar{\nu}_e - \left(v + \frac{1}{2}\right)^2 \bar{\nu}_e x_e \quad (v = 0, 1, 2, \dots) \quad \dots (4)$$

where $\bar{\nu}_e$ is the equilibrium vibrational frequency of the oscillator expressed in wave numbers and x_e is the anharmonicity constant. The higher anharmonic terms are neglected. The first anharmonic term which is retained is small and positive for bond stretching vibrations. The effect of anharmonic term is to crowd more closely the vibrational levels. The energy levels are shown in figure.

Put $v = 0$ in the energy equation we get the zero point energy.

$$\text{i.e.,} \quad \epsilon_0 = \frac{1}{2} \bar{\nu}_e - \frac{1}{4} x_e \bar{\nu}_e$$

$$\text{or} \quad \epsilon_0 = \frac{1}{2} \left(1 - \frac{1}{2} x_e\right) \bar{\nu}_e.$$

Rewriting equation (4) as

$$\epsilon_v = \left[1 - \left(v + \frac{1}{2}\right) x_e\right] \left(v + \frac{1}{2}\right) \bar{\nu}_e \quad \dots (5)$$

Comparing this equation with eqn (2) (energy levels of harmonic oscillator), we get.

$$\bar{\nu}_0 = \left[1 - \left(v + \frac{1}{2}\right) x_e\right] \bar{\nu}_e \quad \dots (6)$$

This shows that the anharmonic oscillator behaves like the harmonic oscillator but with an oscillation frequency which decreases steadily with increasing v .

The selection rules for the anharmonic oscillator are found to be

$$\Delta v = \pm 1, \pm 2, \pm 3$$

..... (7)

Normally only the lines of $\Delta v = \pm 1, \pm 2$ and ± 3 have observable intensity.

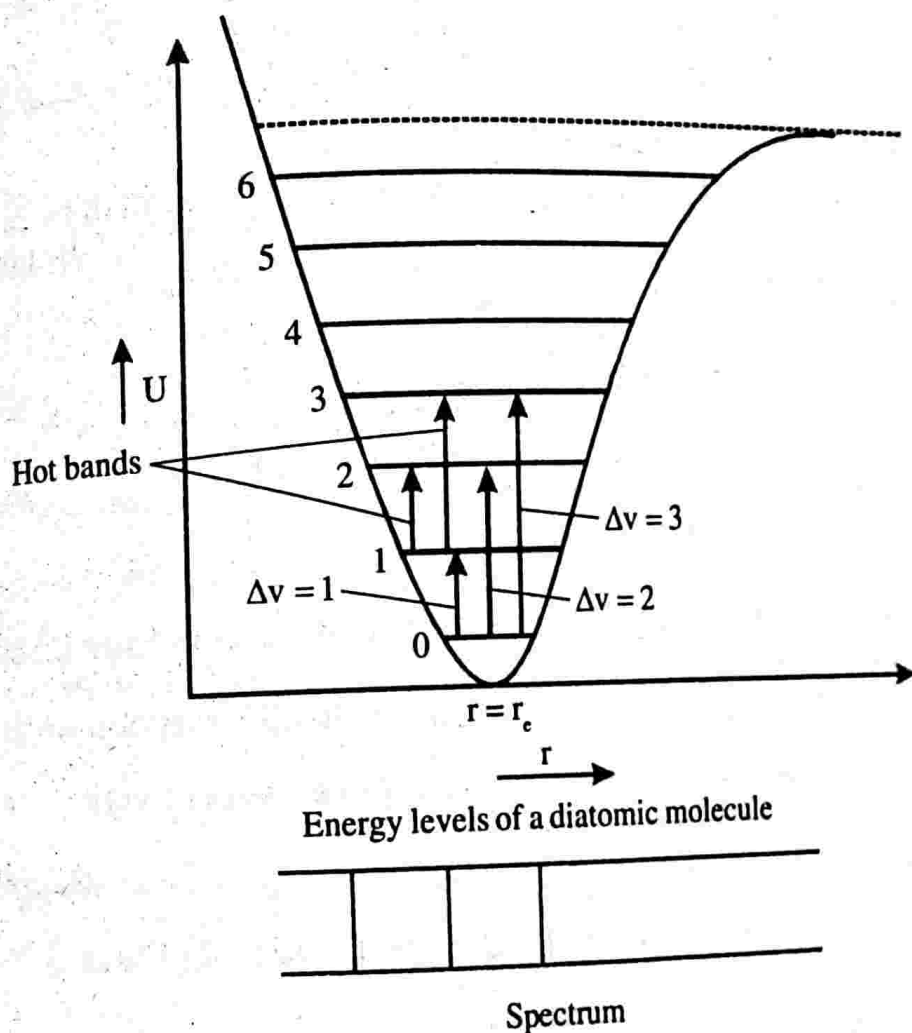


Figure : 5.4

At room temperature nearly all the molecules are in the $v = 0$ state. i.e., the molecules have only the zero point vibrational energy. The absorption of radiation must, therefore, result in transitions starting from $v = 0$.

1. The absorption band corresponds to $v = 0 \rightarrow v = 1$, $\Delta v = +1$, with considerable intensity.

$$\begin{aligned} \Delta E = \epsilon_{v=1} - \epsilon_{v=0} &= \left(1 + \frac{1}{2}\right) \bar{\nu}_e - \left(1 + \frac{1}{2}\right)^2 x_e \bar{\nu}_e - \left[\frac{1}{2} \bar{\nu}_e - \left(\frac{1}{2}\right)^2 x_e \bar{\nu}_e\right] \\ &= (1 - 2x_e) \bar{\nu}_e \end{aligned} \quad \text{..... (8)}$$

2. The absorption band corresponding to $v = 0 \rightarrow v = 2$, $\Delta v = +2$ with small intensity.

$$\begin{aligned}\Delta\varepsilon = \varepsilon_{v=2} - \varepsilon_{v=0} &= \left(2 + \frac{1}{2}\right)\bar{\nu}_e - \left(2 + \frac{1}{2}\right)^2 x_e \bar{\nu}_e - \left[\frac{\bar{\nu}_e}{2} - \left(\frac{1}{2}\right)^2 x_e \bar{\nu}_e\right] \\ &= 2(1 - 3x_e)\bar{\nu}_e\end{aligned}\quad \text{.....(9)}$$

3. The absorption band corresponding to $v = 0 \rightarrow v = 3$, $\Delta v = +3$ with normally negligible intensity.

$$\begin{aligned}\Delta\varepsilon = \varepsilon_{v=3} - \varepsilon_{v=0} &= \left(3 + \frac{1}{2}\right)\bar{\nu}_e - \left(3 + \frac{1}{2}\right)^2 x_e \bar{\nu}_e - \left[\frac{\bar{\nu}_e}{2} - \left(\frac{1}{2}\right)^2 x_e \bar{\nu}_e\right] \\ &= 3(1 - 4x_e)\bar{\nu}_e\end{aligned}\quad \text{..... (10)}$$

Since x_e is very small ($x_e \approx 0.01$), the above three absorption lines lie close to $\bar{\nu}_e$, $2\bar{\nu}_e$ and $3\bar{\nu}_e$. Thus the line near $\bar{\nu}_e$ is called fundamental absorption while those near $2\bar{\nu}_e$ and $3\bar{\nu}_e$ are called the first and second overtones respectively.

To cite an example, the spectrum of H^{35}Cl shows a very intense absorption at 2886cm^{-1} , a weaker one at 5668cm^{-1} and a very weak one at 8347cm^{-1} .

$$\text{i.e., } (1 - 2x_e)\bar{\nu}_e = 2886 \quad \text{..... (1)}$$

$$2(1 - 3x_e)\bar{\nu}_e = 5668 \quad \text{..... (2)}$$

$$3(1 - 4x_e)\bar{\nu}_e = 8347 \quad \text{..... (3)}$$

Solving these we get the equilibrium frequency $\bar{\nu}_e$.

$$\text{eq (2) - eq (1) gives } \bar{\nu}_e - 4x_e \bar{\nu}_e = 2782 \quad \text{..... (4)}$$

$$\text{eq (3) - eq (1) gives } \bar{\nu}_e - 6x_e \bar{\nu}_e = 2679 \quad \text{..... (5)}$$

eq 4×6 - eq 5×4 gives

$$2\bar{\nu}_e = 5976$$

$$\bar{\nu}_e = 2988\text{cm}^{-1}$$

Put this in eq (1), we get

$$(1 - 2x_e) 2988 = 2886$$

$$1 - 2x_e = \frac{2886}{2988} = 0.96586$$

$$2x_e = 1 - 0.96586$$

$$2x_e = 0.03414$$

$$x_e = 0.017$$

Using $\bar{\nu}_e$, we can directly calculate the force constant of HCl molecule.

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

$$\text{or } \frac{\nu}{c} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} \qquad \frac{\nu}{c} = \frac{1}{\lambda} = \bar{\nu}_e$$

$$\bar{\nu}_e = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}$$

Squaring on both sides we get

$$k = 4\pi^2 c^2 \mu \bar{\nu}_e^2$$

$$\therefore k = 4\pi^2 \times (3 \times 10^{10})^2 (2988)^2 \times 1.6261 \times 10^{-27}$$

$$\mu \text{ of HCl} = 1.6261 \times 10^{-27} \text{ kg}$$

$$\therefore k = 516 \text{ Nm}^{-1}.$$

In the above discussion of transitions, we didn't consider the transition from $\nu = 1$ or $\nu = \text{higher levels}$. At normal temperature these levels are empty. But if the temperature is raised or if the vibration has a low frequency, the population of state $\nu = 1$ becomes appreciable. The transitions from higher energy levels with the selection rule $\Delta\nu = 1$ are called hot bands. They are called hot bands since high temperature is one condition for their occurrence. The first hot band corresponds to

$$\nu = 1 \rightarrow \nu = 2; \Delta\nu = +1, \text{ normally very weak.}$$

$$\Delta\varepsilon = \varepsilon_{v=2} - \varepsilon_{v=1} = \left(2 + \frac{1}{2}\right) \bar{\nu}_e - \left(2 + \frac{1}{2}\right)^2 \bar{\nu}_e x_e - \left[\left(1 + \frac{1}{2}\right) \bar{\nu}_e - \left(1 + \frac{1}{2}\right)^2 \bar{\nu}_e x_e \right]$$

$$\Delta\varepsilon = (1 - 4x_e) \bar{\nu}_e \quad \dots (11)$$

Their nature may be confirmed by raising the temperature of the sample when a true hot band will increase in intensity.

Example 1

The fundamental and first overtone transitions of $^{14}\text{N}^{16}\text{O}$ are centred at 1876.06cm^{-1} and 3724.20cm^{-1} respectively. Evaluate the equilibrium vibration frequency, the anharmonicity and the exact zero point energy.

Solution

Given

$$(1 - 2x_e) \bar{\nu}_e = 1876.06 \quad \dots (1)$$

$$2(1 - 3x_e) \bar{\nu}_e = 3724.20 \quad \dots (2)$$

eq (1) \times 3 - eq (2) gives

$$\bar{\nu}_e = 1876.06 \times 3 - 3724.20$$

$$\bar{\nu}_e = 1903.98\text{cm}^{-1}$$

Putting the value of $\bar{\nu}_e$ in eq (1), we get

$$(1 - 2x_e) 1903.98 = 1876.06$$

$$1 - 2x_e = \frac{1876.06}{1903.98} = 0.98534$$

$$2x_e = 1 - 0.98534 = 0.01466$$

$$x_e = \frac{0.01466}{2} = 7.33 \times 10^{-3}$$

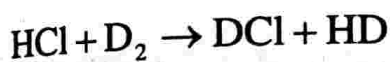
$$\text{Zero point energy } \epsilon_0 = \frac{1}{2} \left(1 - \frac{1}{2} x_e \right) \bar{\nu}_e$$

$$\epsilon_0 = \frac{1}{2} \left(1 - \frac{7.33 \times 10^{-3}}{2} \right) 1903.98$$

$$\epsilon_0 = 948.5 \text{ cm}^{-1}$$

Example 2

The vibrational wave numbers of the following molecules in their $v=0$ states are HCl : 2885 cm^{-1} , DCl : 1990 cm^{-1} , D_2 : 2990 cm^{-1} and HD : 3627 cm^{-1} . Calculate the energy change in kJ mol^{-1} of the reaction.



Solution

$$\text{The zero point energy } \epsilon_0 = \frac{1}{2} \bar{\nu}_e$$

The zero point energy of (HCl + D_2)

$$= \frac{1}{2} (2885 + 2990) = 2937.5 \text{ cm}^{-1}$$

The zero point energy of (DCl + HD)

$$= \frac{1}{2} (1990 + 3627) = 2808.5 \text{ cm}^{-1}$$

$$\therefore \text{Energy released, } \epsilon = 2937.5 - 2808.5 = 129 \text{ cm}^{-1}.$$

To convert this into joules multiply with hc

$$\begin{aligned} \therefore E &= hc \epsilon = 6.626 \times 10^{-34} \times 3 \times 10^{10} \times 129 \\ &= 2564.26 \times 10^{-24} \text{ J} \end{aligned}$$

For one mole the energy released

$$\begin{aligned} E &= 2564.26 \times 10^{-24} \times 6.02 \times 10^{23} \text{ J} = 1.543 \times 10^3 \text{ J/mole} \\ &= 1.543 \text{ kJmole}^{-1} \end{aligned}$$

Infrared spectra-spectral transitions

A molecule is a collection of atoms. The atoms in a molecule execute different types of vibrational motion. The energy of most of these molecular vibrations is quantised and corresponds to that of the infrared region of the electromagnetic spectrum. When infrared radiation of the same frequency is allowed to fall on the molecule, the system absorbs energy causing the excitation of the molecule to higher vibrational levels. The molecules absorbing a quantum of energy give rise to bands characteristics of the molecule from about 50 to $12,500\text{cm}^{-1}$ approximately. This range is generally subdivided into three regions. $12500 - 4000\text{cm}^{-1}$ near IR region, $4000 - 400\text{cm}^{-1}$ middle IR region and $400 - 50\text{cm}^{-1}$ far IR region. The middle IR region is most important since it covers most of the vibrational transitions. The far IR region is important when we deal with solids.

Infrared selection rule

The transition from a vibrational state i to state j is determined by the probability of transition moment given by

$$\mu_{ij} = \int \psi_i^* \mu \psi_j d\tau$$

where ψ_i and ψ_j are the wave functions for the vibrational states i and j and μ is the dipole moment operator. The dipole moment of a molecule is a function of normal coordinates Q_K of the vibrational and can be expanded in a Taylor series.

$$\mu = \mu_0 + \left(\frac{\partial \mu}{\partial Q_K} \right)_0 Q_K + \dots$$

Neglected higher order terms.

$$\therefore \mu_{ij} = \int \psi_i^* \left[\mu_0 + \left(\frac{\partial \mu}{\partial Q_K} \right)_0 Q_K \right] \psi_j d\tau$$

$$\mu_{ij} = \mu_0 \int \psi_i^* \psi_j d\tau + \left(\frac{\partial \mu}{\partial Q_K} \right)_0 \int \psi_i^* Q_K \psi_j d\tau$$

$$\int \psi_i^* \psi_j d\tau = 0 \text{ orthogonality condition.}$$

$$\therefore \mu_{ij} = \left(\frac{\partial \mu}{\partial Q_K} \right)_0 \int \psi_i^* Q_K \psi_j d\tau$$

For the transition to occur the probability of transition moment μ_{ij} must be non zero. For this to occur

$$1. \left(\frac{\partial \mu}{\partial Q_K} \right)_0 \neq 0 \text{ and}$$

$$2. \int \psi_i^* Q_K \psi_j d\tau \neq 0$$

Condition (1) says that at least one component of μ must exist and there must be a change in the dipole moment. Condition (2) says that the integral must be finite. This is possible only if the vibrational quantum number changes by $\Delta v = \pm 1$ under harmonic oscillator and $\Delta v = \pm 1, \pm 2, \pm 3, \dots$ for anharmonic oscillator.

Diatomic vibrating rotator

So far we have considered rotation and vibration of a diatomic molecule separately. But in reality a diatomic molecule possesses both the motion simultaneously. i.e., a molecule rotates while executing vibrational motion and therefore rotational energy changes may also accompany vibrational energy change. As a result we obtain a complex spectra which reflects both rotational and vibrational energy changes. Since the energies of two motions differ considerably, as a first approximation we consider that a diatomic molecule can execute rotations and vibrations quite independently. This is called the Born - Oppenheimer approximation.

The total energy of the diatomic molecule is given by

$$\epsilon_{\text{total}} = \epsilon_{\text{rot}} + \epsilon_{\text{vib}}$$

$$\text{i.e., } \epsilon_{\text{total}} = \epsilon_J + \epsilon_v \text{ in cm}^{-1}.$$

$$\epsilon_{\text{total}} = \epsilon_{Jv} = BJ(J+1) - DJ^2(J+1)^2 + \left(v + \frac{1}{2}\right) \bar{\nu}_e - \left(v + \frac{1}{2}\right)^2 x_e \bar{\nu}_e$$

where $J = 0, 1, 2, \dots$ and $v = 0, 1, 2, \dots$

The selection rule for the combined motions are the same for separate motions

i.e., $\Delta J = \pm 1$ and $\Delta v = \pm 1, \pm 2, \pm 3, \dots$

Now consider the vibrational transition $v = 0 \rightarrow v = 1$. Denoting the upper state by J' and lower state by J'' and assume that Band D are the same for both.

$$\begin{aligned} \therefore \Delta \epsilon_{J,v} = \epsilon_{J',v=1} - \epsilon_{J'',v=0} &= B[J'(J'+1) - J''(J''+1)] - D[J'^2(J'+1)^2 - J''^2(J''+1)^2] \\ &+ \left[\left(1 + \frac{1}{2}\right) \bar{\nu}_e - \left(1 + \frac{1}{2}\right)^2 x_e \bar{\nu}_e \right] - \left[\frac{1}{2} \bar{\nu}_e - \left(\frac{1}{2}\right)^2 x_e \bar{\nu}_e \right] \end{aligned}$$

Using the selection rule $\Delta J = 1 = J' - J''$

Replace all J' with $1 + J''$, we get

$$\begin{aligned} \Delta \epsilon_{J,v} &= B[(1 + J'')(1 + J'' + 1) - J''(J'' + 1)] \\ &- D[(1 + J'')^2 (1 + J'' + 1)^2 - J''^2 (J'' + 1)^2] \\ &+ \frac{3}{2} \bar{\nu}_e - \frac{9}{4} x_e \bar{\nu}_e - \frac{1}{2} \bar{\nu}_e + \frac{1}{4} x_e \bar{\nu}_e \\ \Delta \epsilon_{J,v} &= B[(1 + J'')(2 + J'') - J''(J'' + 1)] \\ &- D\{(1 + J'')^2 [(2 + J'')^2 - J''^2]\} + \bar{\nu}_e - 2x_e \bar{\nu}_e \\ \Delta \epsilon_{J,v} &= B[(2 + J'' + 2J'' + J''^2 - J''^2 - J'')] \\ &- D(1 + J'')^2 [4 + 4J'' + J''^2 - J''^2] + \bar{\nu}_e (1 - 2x_e) \\ \Delta \epsilon_{J,v} &= B2(J'' + 1) - 4D(1 + J'')^3 + \bar{\nu}_e (1 - 2x_e) \end{aligned}$$

The term $(1 - 2x_e) \bar{\nu}_e$ can be recognised to be the frequency of transition from $v = 0 \rightarrow v = 1$ and is denoted by $\bar{\nu}_0$.

$$\therefore \Delta \epsilon_{J,v} = \bar{\nu}_0 + 2B(J'' + 1) - 4D(1 + J'')^3 \text{ with } J'' = 0, 1, 2 \quad \dots (12)$$

Similarly for the selection rule $\Delta J = -1$ i.e., $J' - J'' = -1$ we get

$$\Delta \epsilon_{J,v} = \bar{\nu}_0 - 2B(J' + 1) + 4D(1 + J')^3 \text{ with } J' = 0, 1, 2 \quad \dots (13)$$

Lines corresponding to $\Delta J = -1$ are called the P branch and those corresponding to $\Delta J = +1$ are referred to as R branch.

Lines arising from $\Delta J = -2, -1, 0, +1, +2$ are called O, P, Q, R and S branch respectively.

Combining equations 12 and 13 by replacing $J''+1$, with m in eqn 12 and $J'+1$ with m in eqn 13, we get.

$$\Delta \epsilon_{J,v} = \bar{\nu}_0 + 2Bm - 4Dm^3, \quad m = \pm 1, \pm 2, \pm 3, \dots \quad \dots (14)$$

m takes positive values for $\Delta J = \pm 1$ and negative values for $\Delta J = -1$.

Note that m cannot be zero because if $m = 0$ then $J''+1=0$ or $J'+1=0$ which implies that $J'' = -1$ or $J' = -1$, This is not allowed. The frequency $\bar{\nu}_0$ is usually called the band origin or band centre.

Usually the value of D is very small. This is because the value of B is about 10cm^{-1} or less, while D is only nearly 1% of B . Since a good infrared spectrometer has a resolving power of about 0.5cm^{-1} it is obvious that D is negligibly small. In such cases equation 14 becomes.

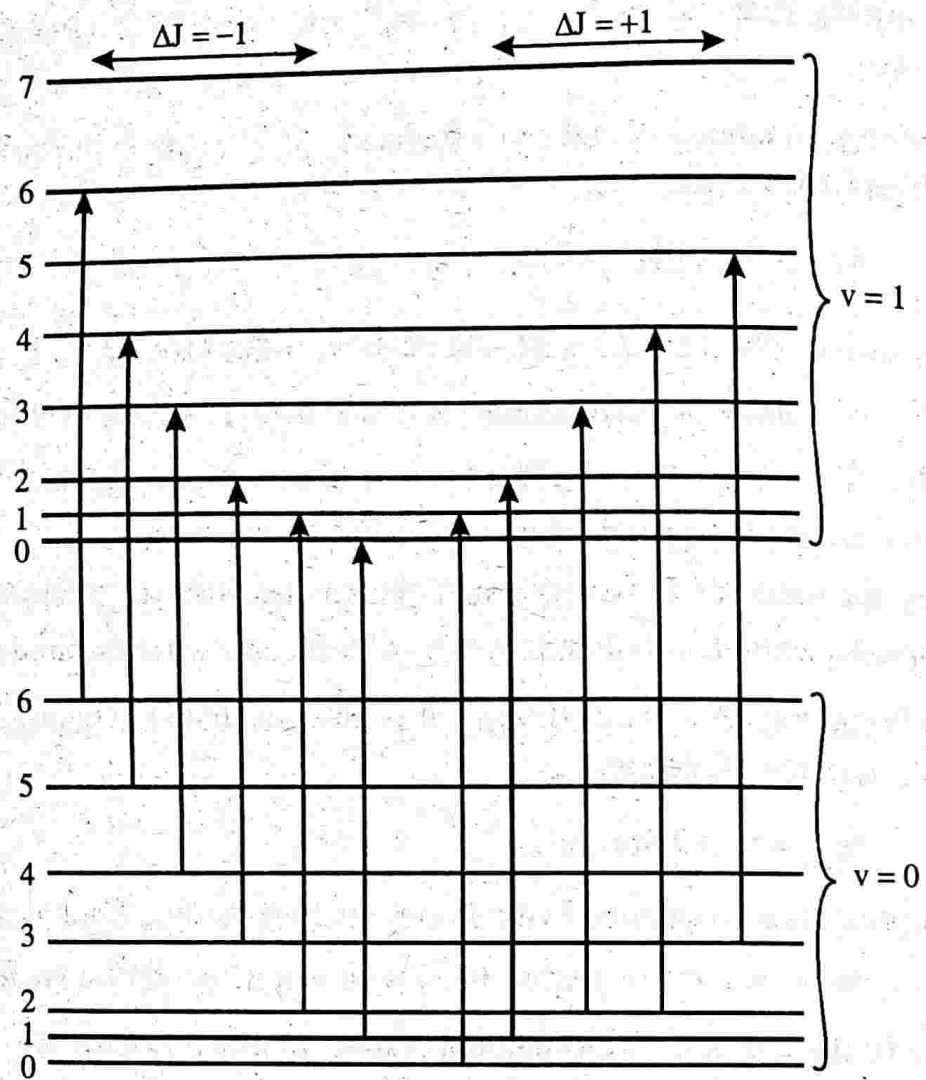
$$\Delta \epsilon_{J,v} = \bar{\nu}_0 + 2Bm \text{ cm}^{-1} \quad \dots (15)$$

This represents the combined vibration rotation spectrum. Such a spectrum will obviously consist of equally spaced lines with a spacing $2B$ on each side of $\bar{\nu}_0$. Since $m \neq 0$, the line at $\bar{\nu}_0$ itself will not appear. If $m \neq 0$, we get $\Delta \epsilon_{J,v} = \bar{\nu}_0$ so we can expect a spectral line. But $m = 0$ is forbidden, because $m = 0$ implies $J'' = -1$ or $J' = -1$ this is not allowed. So $m = 0$ is not allowed. Hence we cannot get spectral lines of $\bar{\nu}_0$.

If we consider a spectrum corresponding to transition from $v = 0 \rightarrow v = 1$, we get two branches (P branch and R branch) on either side of the unseen spectral line corresponding to $\bar{\nu}_0$. P branch corresponds to $\Delta J = -1$ and R branch corresponds to $\Delta J = +1$. See figure below.

These theoretical predictions are in agreement with the experiment.

Further more analysis of the vibration-rotation spectrum of a diatomic molecule allows us one to determine the band $\bar{\nu}_0$ and B from the spacing between the lines. From B , one can calculate the bond length and from $\bar{\nu}_0$ the bond force constant.



Rotational energy levels of the vibrational states $v = 0 \rightarrow v = 1$

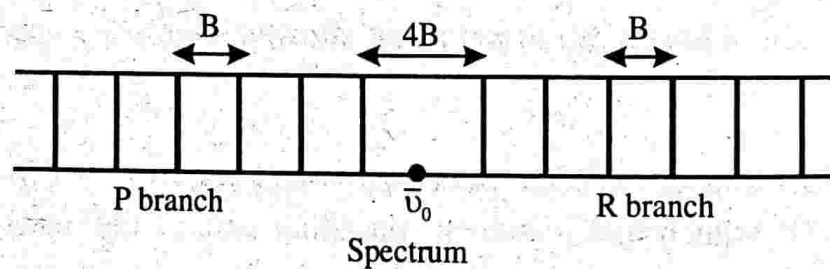


Figure 5.5

Note : - we have $\Delta\epsilon_{J,v} = \bar{\nu}_0 + 2Bm$ when $m = -1$, which corresponds to first P line.

i.e., $\Delta\epsilon_{J,v}^{P_1} = \bar{\nu}_0 - 2B$

when $m = +1$, which corresponds to first R line

i.e., $\Delta\epsilon_{J,v}^{R_1} = \bar{\nu}_0 + 2B$

∴ Separation between first R line and first P line on either side of the $\bar{\nu}_0$ line is

$$\Delta\epsilon_{J_v}^R - \epsilon_{J_v}^P = (\bar{\nu}_0 + 2B) - (\bar{\nu}_0 - 2B) = 4B$$

Similarly for $m = -2$, which corresponds 2nd P line

i.e.,
$$\Delta\epsilon_{J_v}^{R_2} = \bar{\nu}_0 - 4B$$

$$\Delta\epsilon_{J_v}^{P_1} - \Delta\epsilon_{J_v}^{R_2} = (\bar{\nu}_0 - 2B) - (\bar{\nu}_0 - 4B) = 2B$$

When $m = 2$, which correspond to 2nd R line.

$$\Delta\epsilon_{J_v}^{R_2} = \bar{\nu}_0 + 4B$$

$$\Delta\epsilon_{J_v}^{R_2} - \Delta\epsilon_{J_v}^{R_1} = (\bar{\nu}_0 + 4B) - (\bar{\nu}_0 + 2B) = 2B$$

It shows that the spacing between any two adjacent P line or R line is 2B.

Example 3

The fundamental band for HCl is centred at 2886cm^{-1} . Assuming that the inter nuclear distance is 1.276\AA . Calculate the wave number of the first two lines of each P and R branches of HCl.

Solution

$$\bar{\nu}_0 = 2886\text{cm}^{-1}$$

$$r = 1.276\text{\AA} = 1.277 \times 10^{-10}\text{m}$$

$$\begin{aligned} \mu \text{ of HCl} &= \frac{m_{\text{H}} \times m_{\text{Cl}}}{m_{\text{H}} + m_{\text{Cl}}} = \frac{1.008 \times 35.45}{(1.008 + 35.45)} 6.023 \times 10^{26} \\ &= 1.6275 \times 10^{-27}\text{kg} \end{aligned}$$

$$\text{The rotational constant } B = \frac{h}{8\pi^2 \mu r^2 c}$$

$$B = \frac{6.626 \times 10^{-34}}{8 \times \pi^2 \times 1.6275 \times 10^{-27} \times (1.276 \times 10^{-10})^2 \times 3 \times 10^{10}}$$

$$B = 10.6129\text{cm}^{-1}$$

Using

$$(\Delta\epsilon)_{J_v} = \bar{\nu}_0 + 2Bm$$

$$(\Delta\epsilon)_{J_v}^{P_1} = \bar{\nu}_0 - 2B = 2886 - 2 \times 10.6129 = 2864.79\text{cm}^{-1}$$

$$(\Delta\varepsilon)_{J,v}^{P_2} = \bar{\nu}_0 - 4B = 2886 - 4 \times 10.6129 = 2843.55 \text{ cm}^{-1}$$

$$(\Delta\varepsilon)_{J,v}^{R_1} = \bar{\nu}_0 + 2B = 2886 + 6 + 2 \times 10.6129 = 2907.23 \text{ cm}^{-1}$$

$$(\Delta\varepsilon)_{J,v}^{R_2} = \bar{\nu}_0 + 4B = 2886 + 6 + 4 \times 10.6129 = 2928.45 \text{ cm}^{-1}.$$

Example 4

Calculate the energy in cm^{-1} of the absorbed when HCl molecule goes from the state $v=0, J''=1 \rightarrow v=1, J'=0$ and $v=0, J''=1 \rightarrow v=1, J'=2$. Given $\bar{\nu}_e = 2990 \text{ cm}^{-1}$, $x_e = 0.0174$, $r_{\text{HCl}} = 0.1274 \text{ nm}$ and $\mu_{\text{HCl}} = 1.6275 \times 10^{-27} \text{ kg}$.

Solution

$v=0, J''=1 \rightarrow v=1, J'=0$ corresponds to the first line in the P branch

$$\text{So } (\Delta\varepsilon)_{J,v} = (1 - 2x_e)\bar{\nu}_e - 2B$$

$$\text{But } B = \frac{h}{8\pi^2 \mu r^2 c} = \frac{6.626 \times 10^{-34}}{8\pi^2 \times 1.6275 \times 10^{-27} \times (0.1274 \times 10^{-9})^2 \times 3 \times 10^{10}}$$

$$B = 10.589 \text{ cm}^{-1}$$

$$\begin{aligned} \therefore (\Delta\varepsilon)_{J,v}^{P_1} &= (1 - 2 \times 0.0174)2990 - 2 \times 10.589 \\ &= 2885.95 - 21.178 \\ &= 2864.77 \text{ cm}^{-1}. \end{aligned}$$

$v=0, J''=1 \rightarrow v=1, J'=2$ corresponds to the second line in the R branch ($m=2$)

$$\begin{aligned} \therefore (\Delta\varepsilon)_{J,v}^{R_1} &= (1 - 2x_e)\bar{\nu}_e + 4B \\ &= 2885.95 + 42.356 \\ &= 2928 \text{ cm}^{-1}. \end{aligned}$$

IMPORTANT FORMULAE

1. Harmonic oscillator model:

a) Restoring force:

$$f = -k(r - r_e)$$

b) Potential energy:

$$U = \frac{1}{2}k(r - r_e)^2$$

c) Frequency of the oscillator: $\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$ $\mu = \frac{m_1 m_2}{m_1 + m_2}$

2. The vibrational energy of oscillator:

$$E_v = \left(v + \frac{1}{2}\right) h\nu_0, \quad v = 0, 1, 2, 3, \dots$$

or $\epsilon_v = \left(v + \frac{1}{2}\right) \frac{\nu_0}{c}$

$$\epsilon_v = \left(v + \frac{1}{2}\right) \bar{\nu}_0, \quad \bar{\nu}_0 = \frac{1}{\lambda} = \frac{\nu_0}{c}$$

3. Selection rule for harmonic oscillator system: $\Delta v = \pm 1$

4. Morse function:

$$U = D_e \left[1 - e^{-a(r_e - r)} \right]^2$$

5. Vibrational energy levels of a anharmonic oscillator using Morse function:

$$\epsilon_v = \left(v + \frac{1}{2}\right) \bar{\nu}_e - \left(v + \frac{1}{2}\right)^2 \bar{\nu}_e x_e$$

6. Selection rules for the anharmonic oscillator:

$$\Delta v = \pm 1, \pm 2, \pm 3$$

7. Rotational-vibrational energy of a diatomic molecule:

$$\epsilon_{\text{total}} = BJ(J+1) - DJ^2(J+1)^2 + \left(v + \frac{1}{2}\right) \bar{\nu}_e - \left(v + \frac{1}{2}\right)^2 x_e \bar{\nu}_e$$

8. Selection rule for the combined (rotational and vibrational) motions:

$$\Delta J = \pm 1 \quad \text{and} \quad \Delta v = \pm 1, \pm 2, \pm 3$$

9. The spacing between any two adjacent P-lines or R lines = $2B$.

UNIVERSITY MODEL QUESTIONS

Section A

*(Answer questions in two or three sentences)***Short answer type questions**

1. What is infrared spectroscopy?
2. What is vibrational spectra?
3. What is zero point energy? What is its significance?
4. What is rotational quantum number?
5. Write down the selection rule for the harmonic oscillator under going vibrational changes.
6. Write down the expression for the vibrational energy of a harmonic oscillator system and explain the symbols.
7. Draw the allowed vibrational energy levels and transitions between them for a diatomic molecule undergoing simple harmonic motion.
8. Homonuclear diatomic molecules donot show vibrational spectra. Why?
9. Real molecules donot obey exactly the laws of simple harmonic motion. Why?
10. Explain the diatomic molecule as a simple harmonic oscillator model.
11. What is an anharmonic oscillator?
12. What is Morse function?
13. Draw graphical representation of Morse function.
14. Write down the expression for energy eigen value of a diatomic molecule as an anharmonic oscillator.
15. Write down the selection rules for the anharmonic oscillator.
16. What is fundamental absorption of an anharmonic oscillator?
17. What are first and second overtones of absorption of a anharmonic oscillator?
18. What are hot bands? Why are they called so?
19. Explain the formation of IR spectra.
20. What are the selection rules for the infrared spectra?
21. What is Born Oppenheimer approximation?
22. Write down the expression for total energy of a diatomic molecule as a vibrating rotator in terms of wave number and explain the symbols.
23. Explain the P-branch and R branch of a rotation vibration spectrum.
24. Show that the spacing between any two adjacement P lines or R lines is equal to B.
25. Write down the expression for the separation between two maxima of the branches.
26. What are the selection rules for the rotation-vibration spectra.
27. Draw the rotational energy levels of the vibrational states $v = 0 \rightarrow v = 1$.

Section B

(Answer questions in a paragraph of about half a page to one page)

Paragraph / Problem type questions

1. Show that the spacing of vibrational energy levels of a diatomic molecule as a harmonic oscillator are equally spaced.
2. The fundamental and first overtone transitions of CO are centred at 2143.3 cm^{-1} and 4260.0 cm^{-1} . Calculate the equilibrium oscillation frequency, the anharmonicity constant and force constant of the molecule.

$$[\bar{\nu}_e = 2170 \text{ cm}^{-1}, x_e = 0.006124, k = 1905 \text{ Nm}^{-1}]$$
3. The fundamental vibration frequency of HCl is 2989 cm^{-1} . Find the force constant of HCl bond.

$$[516.9 \text{ Nm}^{-1}]$$
4. The vibration frequency of $^1\text{H}^{35}\text{Cl}$ is 2990.6 cm^{-1} without calculating the bond constant estimate the frequency of $^1\text{H}^{37}\text{Cl}$ and $^2\text{D}^{35}\text{Cl}$.

$$[2988 \text{ cm}^{-1}, 2144 \text{ cm}^{-1}]$$
5. The mean intermolecular distance for HCl in the $v = 0$ and $v = 1$ level is 1.293 \AA . Calculate the difference in cm^{-1} between the first P line and the first R line in the rotation - vibration spectrum. Given μ of HCl $= 1.6275 \times 10^{-27} \text{ kg}$.

$$[41.12 \text{ cm}^{-1}]$$
6. Calculate the energy in cm^{-1} of the photon absorbed when NO molecule goes from the state $v = 0, J'' = 0 \rightarrow v = 1, J' = 1$. Assume that the $v = 0$ and $v = 1$ states have the same B values. Given $\bar{\nu}_e = 1904 \text{ cm}^{-1}$, $x_e = 0.00733$, $r_{\text{NO}} = 0.1151 \text{ nm}$ and $\mu_{\text{NO}} = 12.3975 \times 10^{-27} \text{ kg}$.

$$[1879.49 \text{ cm}^{-1}]$$
7. The frequency of OH vibration in CH_3OH is 3300 cm^{-1} . Estimate the frequency of OD stretching vibration in CH_3OD .

$$[2401 \text{ cm}^{-1}]$$

Section C

(Answer questions in about two pages)

Long answer type questions (Essays)

1. Discuss the theory of rotation-vibration spectrum of a diatomic molecule.
2. Discuss the rotational spectra of a diatomic molecule as a (a) harmonic oscillator (b) anharmonic oscillator.

Hints to problems

$$2. (1 - 2x_e)\bar{\nu}_e = 2143.3 \quad \dots (1)$$

$$2(1 - 3x_e)\bar{\nu}_e = 4260.0 \quad \dots (2)$$

$$\frac{\text{eqn 2}}{\text{eqn 1}} \rightarrow \frac{2(1 - 3x_e)}{(1 - 2x_e)} = \frac{4260}{2143.3} = 1.9876$$

$$\text{or } 2 - 6x_e = 1.9876 - 1.9876 \times 2x_e$$

$$2 - 1.9876 = 6x_e - 1.9876 \times 2x_e$$

$$0.0124 = 2.0248x_e$$

$$\therefore x_e = \frac{0.0124}{2.0248} = 6.124 \times 10^{-3}$$

Put this value in eqn (1), we get $\bar{\nu}_e = 2170 \text{ cm}^{-1}$

$$\text{Force constant, } k = 4\pi^2 c^2 \mu \bar{\nu}_e^2$$

$$\mu \text{ of CO} = \frac{m_C \times m_O}{m_C + m_O} = \frac{12 \times 15.9994}{(12 + 15.9994)6.02 \times 10^{26}} = 1.1385 \times 10^{-26} \text{ kg}$$

$$\therefore k = 1904.8 \approx 1905 \text{ Nm}^{-1}$$

$$3. \text{ Using } k = 4\pi^2 c^2 \mu \bar{\nu}_e^2, \bar{\nu}_e = 2989 \text{ cm}^{-1}$$

$$\begin{aligned} \mu \text{ of HCl} &= \frac{m_H \times m_{Cl}}{m_H + m_{Cl}} = \frac{1.673 \times 10^{-27} \times 61.38 \times 10^{-27}}{(1.673 + 61.38) \times 10^{-27}} \\ &= 1.6286 \times 10^{-27} \text{ kg} \end{aligned}$$

$$\therefore k = 516.9 \text{ Nm}^{-1}$$

$$4. \text{ We have } \bar{\nu}_e = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

$$\text{or } \bar{\nu}_e \propto \frac{1}{\sqrt{\mu}}$$

$$\therefore \frac{(\bar{\nu}_e)_{H^{37}Cl}}{(\bar{\nu}_e)_{H^{35}Cl}} = \sqrt{\frac{\mu_{35}}{\mu_{37}}} = \sqrt{\frac{m_H \times {}^{35}m_{Cl}}{m_H + {}^{35}m_{Cl}}} \times \frac{m_H + {}^{37}m_{Cl}}{m_H \times {}^{37}m_{Cl}} = \sqrt{\frac{35}{36} \times \frac{38}{37}} = 0.9992$$

$$\begin{aligned} \therefore (\bar{\nu}_e)_{H^{37}Cl} &= 0.9992 \times 2990.6 \\ &= 2987.9 \approx 2988 \text{ cm}^{-1} \end{aligned}$$

Similarly the other one

$$5. \text{ Using } B = \frac{h}{8\pi^2 \mu r^2 c}$$

Put $c = 3 \times 10^{10} \text{ cm s}^{-1}$ so B will be in cm^{-1} .

We get $B = 10.28 \text{ cm}^{-1}$ our requirement is $4B$.

6. The transition $v = 0, J'' = 0 \rightarrow v = 1, J' = 1$ corresponds to the first line in the R branch.

$$\Delta \varepsilon = (1 - 2x_e) \bar{\nu}_e + 2B$$

$$\text{where } B = \frac{h}{8\pi^2 \mu r^2 c}$$

$$7. \quad \bar{\nu} \propto \sqrt{\mu}$$

$$\therefore \frac{\bar{\nu}_{\text{OD}}}{\bar{\nu}_{\text{OH}}} = \sqrt{\frac{\mu_{\text{OD}}}{\mu_{\text{OH}}}} = \sqrt{\frac{16 \times 2}{16 + 2} \times \frac{16 + 1}{16 \times 1}} = 1.3744$$

$$\therefore \bar{\nu}_{\text{OD}} = 1.3744 \bar{\nu}_{\text{OH}}$$